Crystal and molecular structure of the discogen bis [(1-4-*n*-heptylphenyl,3-4-*n*-heptyloxyphenyl)propane-1,3-dionato] copper(II)

K. Usha[a]; Kalyani Vijayan[b]

[a] Raman Research Institute, Bangalore, India [b] Materials Science Division, National Aeronautical Laboratory, Bangalore, India

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by K. USHA*

Raman Research Institute, Bangalore 560 080, India
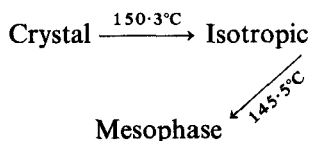
and KALYANI VIJAYAN

Materials Science Division,
National Aeronautical Laboratory, Bangalore 560 017, India

Discotic bis[(1-4-*n*-heptylphenyl,3-4-*n*-heptyloxy-phenyl)propane-1,3-dionato] copper(II) with dissimilarly substituted ligands, crystallizes in the triclinic space group P$\bar{1}$ with two molecules in a unit cell of dimensions $a = 10\cdot228(7)$ Å, $b = 16\cdot607(5)$ Å, $c = 18\cdot273(6)$ Å, $\alpha = 64\cdot40(2)°$, $\beta = 78\cdot53(6)°$ and $\gamma = 72\cdot66(5)°$. The crystal structure was solved by direct methods and refined by full matrix least squares procedure to R of $0\cdot081$. It is established conclusively that similar chains in the molecule are *cis* with respect to the core. The copper atom is significantly displaced from the plane of the coordinating oxygen atoms. The centrosymmetrically related molecules in the unit cell tend to pair. The molecular arrangement in the crystal is layer-like.

1. Introduction

As part of a systematic study on discogens containing transition metal atoms, we have earlier reported [1–3] the crystal and the molecular structures of discogens containing copper and palladium atoms (I, II and III in figure 1). The results indicate that the presence or absence of the oxygen atoms in the chains plays an important role in the molecular packing in the crystal structure. For example, for II and III both of which have only alkyl chains, the molecular arrangements are very similar, but different from that of I, which has four oxygen atoms surrounding the core. Here, we report the crystal structure analysis of yet another copper containing discogen, in which only two of the four chains are chemically identical (IV of figure 1). With two heptyl and two heptyloxy chains [4], the fringe surrounding the core has only two oxygen atoms. The principal aim of this investigation is to compare the molecular geometry and packing of this dissimilarly substituted discogen with those of I, II and III. The transition temperatures [4] of IV are

$$\text{Crystal} \xrightarrow{150\cdot3°C} \text{Isotropic}$$

Mesophase

*Author for correspondence.

(I)   M = Cu $R_1 = R_2 = R_3 = R_4 = OC_8H_{17}$

(II)   M = Pd $R_1 = R_2 = R_3 = R_4 = C_{10}H_{21}$

(III) M = Cu $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

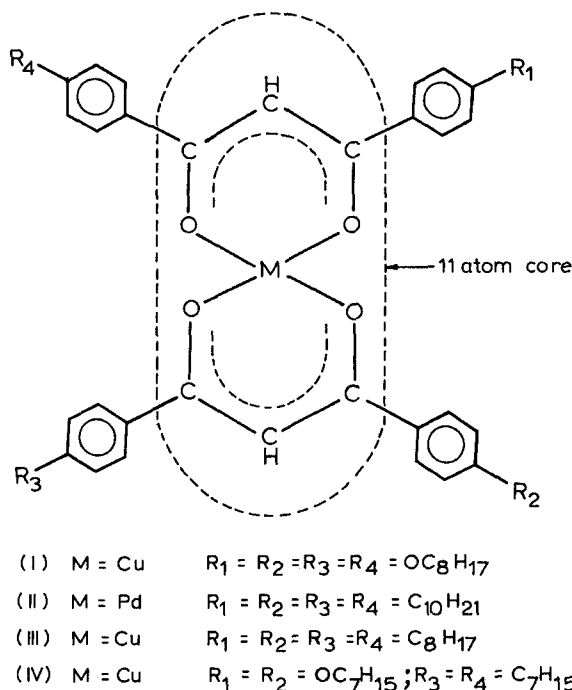(IV)   M = Cu $R_1 = R_2 = OC_7H_{15}$; $R_3 = R_4 = C_7H_{15}$

Figure 1.   Structural formula.

2. Experimental details

Transparent, green coloured, prismatic crystals were obtained by slow evaporation from a solution in butan-2-one. Preliminary, partial characterization of the crystal was done using oscillation and Weissenberg photographs. The unit cell dimensions were determined and refined on a CAD-4 single crystal diffractometer by a least squares method using 25 reflections. Table 1 lists the crystal data and other details relevant to the three dimensional intensity data.

3. Structure determination

The statistical distribution of the normalized structure factors indicated the space group to be centric, which in this case is P$\bar{1}$. The crystal structure was solved by direct methods and refined by a full matrix least squares procedure using anisotropic thermal parameters for all of the non-hydrogen atoms. The hydrogen atoms were placed at their calculated positions using a C–H distance of 1·08 Å [7] and were assigned the equivalent isotropic temperature factor, U_{eq} [8], of the respective carbon atoms to which they are attached. The parameters of the hydrogen atoms were not refined, but their contribution to the structure factors were included in the least squares refinement. Further details of the refinement procedure are listed in table 1.

4. Results and discussion

Figure 2 shows the atomic numbering scheme. The positional and thermal parameters have been deposited with the British Library, copies of the table which comprise two pages may be obtained from the British Library, Lending Division, by quoting the number SUP 16521 according to the procedure described at the end of this issue. The average U_{eq} values for the core and the phenyl rings A to D are 0·084(7) Å^2,

Table 1. Crystal data and other relevant details of the analysis.

Molecular formula	$C_{58}O_6H_{78}Cu$
Molecular weight	934·74
$a/\text{Å}$	10·228(7)
$b/\text{Å}$	16·607(5)
$c/\text{Å}$	18·273(6)
$\alpha/°$	64·40(2)
$\beta/°$	78·53(6)
$\gamma/°$	72·66(5)
$V/\text{Å}^3$	2663
Z	2
Spacegroup	P$\bar{1}$
$\rho_{calc}/\text{g cm}^{-3}$	1·158
$\lambda_{CuK_\alpha}/\text{Å}$	1·5418
$\mu_{CuK_\alpha}/\text{cm}^{-1}$	9·548
Scan mode	$\omega/2\theta$
Scan speed/$°\text{min}^{-1}$	5·5
Standard reflections	3 checked once in 3600 s
Number of unique reflections	6595
Number of reflections used for refinement	2112 with $I \geqslant 3\sigma(I)$
h_{min}	0
h_{max}	10
k_{min}	−16
k_{max}	17
l_{min}	−18
l_{max}	19
Corrections applied	Lp, absorption [5], anomalous scattering [6] for Cu
Scattering factors	C, O [9]
	H [10]
	Cu [6]
Program used for structure solution	MULTAN-80 [11]
Program used for refinement	SHELX-76 [12]
Weighting scheme (w)	$K/(\sigma^2(F) + g(F)^2$
	$K = 3·0192$
	$g = 0·00116$
R	0·0812
R_w	0·0849

0·082(9) Å^2, 0·079(8) Å^2, 0·10(1) Å^2 and 0·10(1) Å^2, respectively. The chains A to D are characterized by U_{eq} values of 0·13(1) Å^2, 0·13(1) Å^2, 0·10(1) Å^2 and 0·16(1) Å^2, respectively. In the residual electron density map computed at the end of the refinement, the highest and the lowest electron densities were 0·32 and −0·31 el/Å^3, respectively. The listing of the final structure factors is available from the authors.

4.1. Molecular conformation

From simple geometric considerations of molecular stability, it would appear that in (IV), the chemically identical chains assume a *trans* arrangement with respect to the core. Interestingly in the crystal structure, they are found to be *cis* with respect to the core. This result though unexpected is conclusive. On examination of the crystals in the dish, it was noted that there are in fact crystals with three different morphologies. It is proposed to analyse the crystal structures and also carry out thermal studies of the
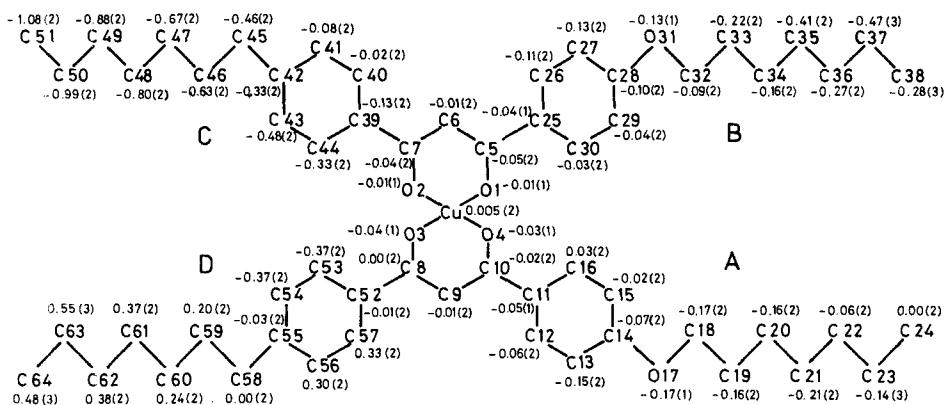
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Figure 2.   The displacement, $\delta/\text{Å}$ of non-hydrogen atoms from the least squares plane through the eleven atom core of the molecule.

other forms to find out if they represent structures with a *trans* conformation. These will be taken up at a later stage.

It may be mentioned that in the crystal structures of a few other mesogens, the dissimilarly substituted ligands are *trans* [13–17]. This analysis provides the first conclusive evidence for the *cis* arrangement of dissimilar chains in a discogen. It may also be mentioned that in the crystal structure of bis[1-thia-4-7-diaza cyclononane) cobalt (III), which is not mesogenic, molecular mechanics calculations have shown [18] that the *cis* isomer is more stable than the corresponding *trans* isomer. Therefore, it appears that the occurrence of a stable *cis* form in crystals is not an uncommon feature.

Figure 3 represents the stereo diagram of the molecules in the unit cell viewed down the *a* axis. It is found that all of the four chains are fully extended away from the core and assume an all-*trans* configuration.

4.2. Molecular geometry

Within the limits of experimental error, the molecular dimensions listed in table 2 are normal. The copper atom is significantly displaced from the plane of the
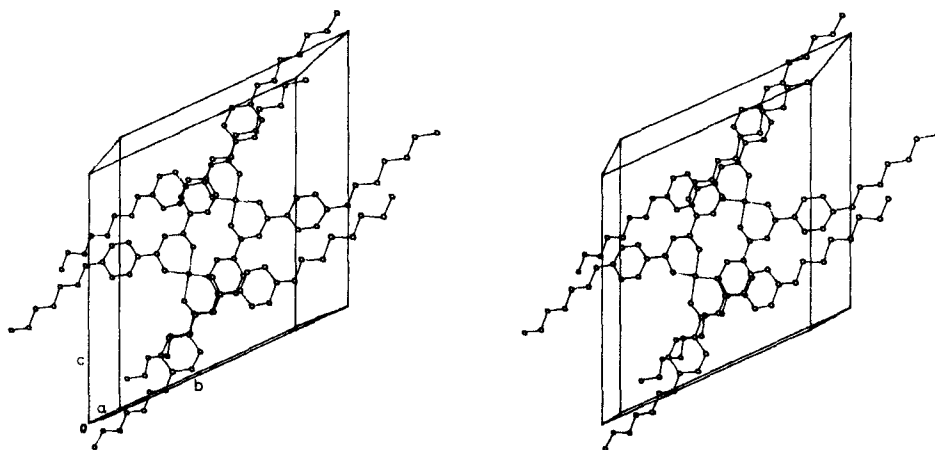
Figure 3.   Stereo diagram of the molecules in the unit cell viewed down the *a* axis.

coordinating oxygen atoms, the displacement being 0·027(2) Å. This feature is in striking contrast with the in-plane arrangement of the metal atom observed in the crystal structures of the discogens (I), (II) and (III) in figure 1. Figure 2 shows the displacement, δ, of atoms from the least squares plane through the eleven atom core. As in the case of copper complex (I) where the metal atom occupies a general position, the two halves of the core, *viz*, Cu, O(1), O(2), C(5) to C(7) and Cu, O(3), O(4), C(8) to C(10), are slightly tilted with respect to each other, the angle of tilt being 1·4°. The planar phenyl rings A, B, C and D (see figure 2) are tilted with respect to the core by 3, 2, 10 and 17°, respectively. The tilts are controlled primarily by steric interactions. Conspicuously, the tilts of the phenyl rings A and B substituted with the heptyloxy chains are less than those of the rings C and D substituted with the less heavy heptyl chains. The chains A to D are found to be inclined to the core by 2, 9, 5 and 7°, respectively.

The end-to-end dimensions of the molecule calculated from the distances between the respective terminal atoms, *viz*. C(24)...C(64), C(38)...C(51), C(24)...C(38) and

Table 2. Final bond lengths and bond angles. The quantities in parentheses represent the respective standard deviation.

Bond lengths/Å			
CU–O(1)	1·87(1)	C(29)–C(30)	1·37(3)
CU–O(3)	1·89(1)	O(31)–C(32)	1·44(2)
CU–O(4)	1·90(1)	C(32)–C(33)	1·55(3)
CU–O(2)	1·93(1)	C(33)–C(34)	1·54(2)
O(1)–C(5)	1·23(2)	C(34)–C(35)	1·52(3)
O(2)–C(7)	1·27(2)	C(35)–C(36)	1·55(3)
O(3)–C(8)	1·30(2)	C(36)–C(37)	1·40(4)
O(4)–C(10)	1·30(2)	C(37)–C(38)	1·46(4)
C(5)–C(6)	1·45(2)	C(39)–C(40)	1·35(2)
C(6)–C(7)	1·38(3)	C(39)–C(44)	1·38(3)
C(7)–C(39)	1·53(2)	C(40)–C(41)	1·38(3)
C(8)–C(9)	1·45(2)	C(41)–C(42)	1·36(3)
C(8)–C(52)	1·49(3)	C(42)–C(43)	1·41(2)
C(9)–C(10)	1·30(2)	C(42)–C(45)	1·44(3)
C(10)–C(11)	1·56(2)	C(43)–C(44)	1·40(3)
C(11)–C(16)	1·29(3)	C(45)–C(46)	1·47(3)
C(11)–C(12)	1·42(2)	C(46)–C(47)	1·54(3)
C(12)–C(13)	1·36(3)	C(47)–C(48)	1·49(3)
C(13)–C(14)	1·45(3)	C(48)–C(49)	1·56(3)
C(14)–C(15)	1·37(2)	C(49)–C(50)	1·48(3)
C(14)–O(17)	1·37(2)	C(50)–C(51)	1·53(3)
C(15)–C(16)	1·40(3)	C(52)–C(53)	1·39(3)
O(17)–C(18)	1·48(2)	C(52)–C(57)	1·39(2)
C(18)–C(19)	1·53(3)	C(53)–C(54)	1·38(3)
C(19)–C(20)	1·56(3)	C(54)–C(55)	1·36(2)
C(20)–C(21)	1·51(3)	C(55)–C(56)	1·37(3)
C(21)–C(22)	1·50(3)	C(55)–C(58)	1·40(3)
C(22)–C(23)	1·59(3)	C(56)–C(57)	1·38(3)
C(23)–C(24)	1·40(4)	C(58)–C(59)	1·45(3)
C(25)–C(26)	1·37(2)	C(59)–C(60)	1·47(3)
C(25)–C(30)	1·37(2)	C(60)–C(61)	1·54(3)
C(26)–C(27)	1·32(3)	C(61)–C(62)	1·42(4)
C(27)–C(28)	1·42(2)	C(62)–C(63)	1·57(4)
C(28)–C(29)	1·39(2)	C(63)–C(64)	1·37(5)
C(28)–O(31)	1·40(3)		

Table 2 (*continued*).

Bond angles/°			
O(1)–CU–O(3)	177·6(4)	C(26)–C(27)–C(28)	119(1)
O(1)–CU–O(4)	86·2(4)	C(29)–C(28)–O(31)	128(2)
O(1)–CU–O(2)	92·8(4)	C(29)–C(28)–C(27)	120(2)
O(3)–CU–O(4)	92·3(4)	O(31)–C(28)–C(27)	112(1)
O(3)–CU–O(2)	88·7(4)	C(30)–C(29)–C(28)	117(1)
O(4)–CU–O(2)	178·3(4)	C(29)–C(30)–C(25)	125(1)
C(5)–O(1)–CU	129(1)	C(28)–O(31)–C(32)	114(1)
C(7)–O(2)–CU	125(1)	O(31)–C(32)–C(33)	108(1)
C(8)–O(3)–CU	128(1)	C(34)–C(33)–C(32)	111(1)
C(10)–O(4)–CU	126(1)	C(35)–C(34)–C(33)	110(1)
O(1)–C(5)–C(6)	125(2)	C(34)–C(35)–C(36)	109(2)
O(1)–C(5)–C(25)	119(1)	C(37)–C(36)–C(35)	110(2)
C(6)–C(5)–C(25)	116(1)	C(36)–C(37)–C(38)	116(2)
C(7)–C(6)–C(5)	121(1)	C(40)–C(39)–C(44)	116(2)
O(2)–C(7)–C(6)	127(1)	C(40)–C(39)–C(7)	123(1)
O(2)–C(7)–C(39)	111(1)	C(44)–C(39)–C(7)	121(1)
C(6)–C(7)–C(39)	123(1)	C(39)–C(40)–C(41)	122(2)
O(3)–C(8)–C(9)	122(1)	C(42)–C(41)–C(40)	125(2)
O(3)–C(8)–C(52)	116(1)	C(41)–C(42)–C(43)	113(2)
C(9)–C(8)–C(52)	122(1)	C(41)–C(42)–C(45)	127(2)
C(10)–C(9)–C(8)	123(1)	C(43)–C(42)–C(45)	119(2)
C(9)–C(10)–O(4)	128(2)	C(44)–C(43)–C(42)	122(2)
C(9)–C(10)–C(11)	122(1)	C(39)–C(44)–C(43)	122(2)
O(4)–C(10)–C(11)	110(1)	C(42)–C(45)–C(46)	120(2)
C(16)–C(11)–C(12)	121(1)	C(45)–C(46)–C(47)	114(1)
C(16)–C(11)–C(10)	119(1)	C(48)–C(47)–C(46)	111(1)
C(12)–C(11)–C(10)	120(1)	C(47)–C(48)–C(49)	114(1)
C(13)–C(12)–C(11)	119(1)	C(50)–C(49)–C(48)	117(2)
C(12)–C(13)–C(14)	120(2)	C(49)–C(50)–C(51)	118(2)
C(15)–C(14)–O(17)	129(1)	C(53)–C(52)–C(57)	116(2)
C(15)–C(14)–C(13)	118(2)	C(53)–C(52)–C(8)	119(1)
O(17)–C(14)–C(13)	113(1)	C(57)–C(52)–C(8)	125(1)
C(14)–C(15)–C(16)	119(1)	C(54)–C(53)–C(52)	123(2)
C(11)–C(16)–C(15)	123(1)	C(55)–C(54)–C(53)	120(2)
C(14)–O(17)–C(18)	114(1)	C(54)–C(55)–C(56)	117(2)
O(17)–C(18)–C(19)	109(1)	C(54)–C(55)–C(58)	124(2)
C(18)–C(19)–C(20)	110(1)	C(56)–C(55)–C(58)	119(2)
C(21)–C(20)–C(19)	110(1)	C(55)–C(56)–C(57)	123(2)
C(22)–C(21)–C(20)	107(1)	C(56)–C(57)–C(52)	120(2)
C(21)–C(22)–C(23)	102(2)	C(55)–C(58)–C(59)	121(2)
C(24)–C(23)–C(22)	105(2)	C(58)–C(59)–C(60)	1192)
C(26)–C(25)–C(30)	117(1)	C(59)–C(60)–C(61)	119(2)
C(26)–C(25)–C(5)	129(1)	C(62)–C(61)–C(60)	121(2)
C(30)–C(25)–C(5)	114(1)	C(61)–C(62)–C(63)	115(2)
C(27)–C(26)–C(25)	124(1)	C(64)–C(63)–C(62)	120(2)

C(51)... C(64), are 28·5 Å, 28·8 Å, 9·94 Å and 10·62 Å, respectively. For the discogens (I), (II) and (III), similar end-to-end dimensions represented a more rectangular molecular shape. The slight asymmetry in the widths (9·94 Å and 10·62 Å) observed in this molecule is a consequence of the difference in the lengths of the heptyl and the heptyloxy chains and the *cis* arrangement. The common feature observed in the crystal structures of discogens (I) to (IV) is that these molecules with a length-to-width ratio of

about 3 resemble the model B proposed by Ohta *et al.* [19] for $Cu-OC_8H_{17}$. The repeated observation of model B in these crystal structures suggests that Ohta's model B is perhaps more stable than model A [19] where the length-to-width ratio is about 1. Thus the overall molecular shape in these crystal structures is close to a rectangular disc.

4.3. *Molecular arrangement*

Figure 4 shows the arrangement of the molecules in the plane perpendicular to the crystallographic *a* axis. In the unit cell, although adjacent cores related by a centre of inversion are well separated, the phenyl rings A and B exhibit partial overlap over the phenyl rings of the centrosymmetrically related molecule. The overlapping phenyl rings are found to be substituted with heptyloxy chains. The possible role of the oxygen atoms in favouring the molecular overlap cannot therefore be ignored. Examination of the intermolecular contact distances shows that the contact distances $\leqslant 4$ Å are conspicuously concentrated between the atoms of the centrosymmetrically related molecules in the unit cell. These features suggest that these centrosymmetrically related molecules tend to pair primarily by van der Waals' interactions and perhaps to some extent by partial π-electron overlap. Each of the centrosymmetrically related pairs is surrounded by four others situated at $\pm\vec{b}$ and $\pm\vec{c}$, respectively. A molecular
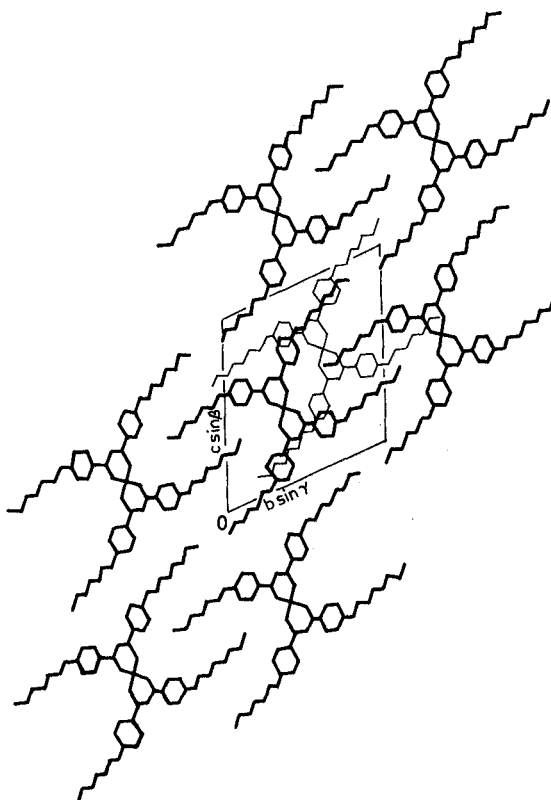

Figure 4. Molecular arrangement in the plane perpendicular to the *a* axis. The thin lines represent the centrosymmetrically related molecule in the unit cell. For the sake of clarity, the translation equivalents of this molecule have been omitted.

coordination number of four is indeed not representative of a close packed arrangement [20]. It may be mentioned that pairing of the centrosymmetrically related molecules was observed earlier in the crystal structure of the discogen $Cu-OC_8H_{17}$ [1] where the cores themselves exhibit substantial overlap.

Figure 4 shows that the arrangement of the molecules is essentially layer-like with the molecules tilted with respect to the plane perpendicular to the crystallographic a axis. The early work of Chandrasekhar et al. [21] has shown that in the mesophase, the arrangement of discogens is columnar. Our earlier X-ray work on discogens [1–3] has shown that the crystalline phase of discogens is also characterized by a columnar arrangement of molecules. This investigation, however, provides evidence that the molecular arrangement in the crystalline phase of a discogen is not necessarily columnar.

Another interesting observation concerns the similarities in the structural characteristics of (IV) with those of a few other mesogens with dissimilarly substituted ligands [13, 15, 16]. In these crystal structures, the metal atoms are displaced from the respective plane of the coordinating atoms and the molecules are arranged in layers. Further evidence for any correlation between (i) dissimilarly substituted ligands and such displacement of the metal atoms and (ii) deviations from strict planarity of the central group of the core and the absence of a columnar arrangement, can be obtained only when data from a larger number of crystal structural investigations are available.

Figure 4 also shows that in the crystal structure of (IV), a striking concentration of aromatic groups around the inversion centre at 1/2, 1/2, 1/2 occurs. The pocket formed by the aromatic groups extends infinitely along the crystallographic a direction and it includes the non-bonded interactions between the centrosymmetrically related molecules. A similar concentration of aliphatic chains is found around the inversion centre at 0, 0, 0.

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